

PATENT SPECIFICATION

DRAWINGS ATTACHED

1069.168



1069.168

Date of Application and filing Complete Specification: Oct. 30, 1964.

No. 44467/64.

Application made in United States of America (No. 384615) on July 23, 1964.

Complete Specification Published: May 17, 1967.

© Crown Copyright 1967.

Index at acceptance:—B2 K(1BY, 1C1, 2A, 2E, 2Y, 3C, 3D, 5A, 5C, 5D, 6A, 7A1, 7AY, 8D, 8F, 9Q3, 9QY); A4 A(1B4A, 1B6, 2A, 2B, 4D, 6E); C7 B(2F, 13, 15X, 16X)

Int. Cl.:—B 05 c//A 47 j

COMPLETE SPECIFICATION

Composite Coated Aluminium Articles

We, GENERAL MAGNAPLATE CORPORATION, a corporation organised under the laws of the State of New Jersey, United States of America, of Belleville, State of New Jersey, United States of America, do hereby declare the invention for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

This invention is directed to composite coated aluminum articles.

In its broadest aspects, the invention relates to composite coated aluminum articles having an aluminum base, an intermediate layer of an irregular, coarsely-crystalline aluminum oxide integral with the metal base, and an outer fluorinated hydrocarbon polymer layer, the polymer extending into the interstices of the oxide layer. (In this Specification, the word "aluminum" insofar as it refers to articles of this metal includes articles of aluminum alloys).

The coated articles are produced by a process which comprises the following steps:—

- (i) cleaning the surface of an aluminum substrate,
- (ii) anodically oxidising the cleaned substrate in an aqueous electrolyte containing from 15 to 18 ounces per gallon of sulphuric acid at a temperature from 25° to 40° F., at least one cubic foot of air per gallon of electrolyte per minute being passed through the electrolyte, the impressed voltage between the cathode and the aluminum anode being from 24 to 90 volts and the anode current density from 25 to 60 amps/sq. ft. the oxidation being continued until the oxide layer is at least 0.005 inch thick.

[Pric

- (iii) immersing the oxidised aluminum in an aqueous suspension of a fluorinated hydrocarbon polymer the particles of said polymer being up to 2 microns in diameter, the suspension being at a temperature of at least 140° F., until the polymer fills the interstices of the oxide layer and forms an outer coating at least 0.0001 inch thick.

The process of the invention is employed for the preparation of composite aluminum articles having a fluorinated hydrocarbon polymer surface. The process is applicable to a wide range of available aluminum alloys, including wrought, cast and forged aluminum. The aluminum metal surface is first cleaned to remove dirt, smut, oxide coating, etc. by suitable methods for preparing aluminum for anodizing. The cleaning treatment varies for different aluminum alloys. A suitable treatment for many aluminum alloys is immersion in a hot sodium hydroxide solution, e.g., containing about 5 to 6 ounces per gallon of sodium hydroxide, for up to one minute followed by one minute immersion in a chromic acid-nitric acid aqueous solution to remove surface smut. The part is then rinsed to remove the cleaning solution.

The irregular, coarsely crystalline, porous coating integral with the aluminum surface is grown upward and outward from the surface of the aluminum base by anodic treatment of the aluminum in a cold, oxidizing sulfuric acid bath utilizing relatively high voltages and high current densities, to obtain a highly absorptive oxide layer at least 0.0005 inch and preferably at least 0.001 inch. For special purposes, the oxide layer may be made thicker, e.g., 0.002 inch. When the desired oxide layer has been obtained, the article is removed from the acid tank, rinsed, and dipped into an aqueous suspension containing a finely subdivided (particle diameter up to

2 micron) fluorinated hydrocarbon polymeric material, and maintained in the suspension until the interstices in the oxide layer are filled with the polymeric material and a top surface coating of at least 0.0001 inch and preferably 0.0002 inch is formed.

The oxidizing sulfuric acid electrolyte contains from 15 to 18 ounces per gallon of sulfuric acid. The baths also preferably contain a carboxylic acid such as oxalic acid or equivalent acids, e.g., malonic acid or succinic acid, in amounts preferably up to about 1/5 the concentration of the sulfuric acid. A sugar, e.g., sucrose in small amounts may also be included in the bath. During the formation of the oxide coating, the bath is highly agitated. It is also important that the bath contain relatively high concentrations of dissolved oxygen and preferably also dissolved carbon dioxide. This is accomplished by passing large quantities of air, e.g., one cubic foot (or more) per minute of air per gallon of solution, through the bath to provide the agitation and to supply the gases to the bath.

The bath is operated at temperatures between 25° F and 40° F. The preferred temperature varies somewhat for different aluminum alloys. Between 30° F and 35° F is a preferred temperature for treating most of the aluminum alloys in greatest commercial demand. The oxidation process usually requires at least 20 minutes and may be as much as one hour and a half, dependent upon the alloy being treated, the current density and voltage utilized, the desired oxide thickness, etc. The voltage utilized varies from 24 to 90 volts. The amperage may vary from 25 amps/sq. ft. to 60 amps/sq. ft., and is preferably 25 amps/sq. ft. to 40 amps/sq. ft. The initial desired current density is obtained on the aluminum metal surface at relatively low voltages. The anodising may be commenced at a voltage below 24 volts provided that the voltage is later stepped up to a value within the specified range.

As the oxide coating is formed and grown or built up, the electrical resistance increases markedly requiring substantially higher voltages to obtain the requisite current densities. Consequently, the voltage is periodically stepped up during most of the processing cycle. The use of stepped voltage and the high current density causes the growth of elongated alumina crystals. Upon removal from the oxide-forming bath, the article is rinsed in cold water, generally for about 15 minutes, until the acid remaining in the interstices of the crystals and pores is removed and/or neutralized. The wet article is then immersed in the fluorinated hydrocarbon polymer impregnation tank.

The impregnation tank contains an aqueous suspension of the fluorinated hydrocarbon polymer. The concentration of the polymeric material in the suspension may vary widely.

As little as one pound of polymeric material per 100 pounds of water has been found to be operative. The preferred operating range is at about one pound of the polymeric material to between 15 and 20 pounds of water. Higher concentrations, for example, up to a 1:1 weight ratio, are operative. However, at higher concentrations, processing difficulties are encountered attributable to the syrup-like characteristics of the bath. The polymeric material should be finely subdivided so that it will be absorbed by and packed by molecular attraction into the fine interstices and pores of the absorptive coarsely crystalline aluminum oxide. For this purpose, particles up to about 2 microns in size are used. It is preferred that the particle size be below 1 micron. Useful results have been obtained with available dispersions having particles of .02 microns and less.

The polymer impregnation tank is operated at temperatures from 140° F up to the boiling temperature and preferably between 160° F and 190° F. The immersion time is preferably between about 20 and 30 minutes to obtain the desired surface, about 0.0002 inch thick. Less time, e.g. 12 minutes, at the higher temperatures may be utilized. Longer immersion time results in the build-up of the layer to thicknesses such as 0.0003 inch or 0.0005 inch.

The materials referred to as "fluorinated" and utilized in the present invention, are fluorine-containing hydrocarbon homopolymers and co-polymers. These include polytetrafluoroethylene and tetrafluoroethylene-hexafluoropropylene co-polymers. The polytetrafluoroethylene is preferred and is sold by the E. I. Du Pont de Nemours & Company under the trademark "TEFLON".

The fluorinated hydrocarbon surfaced article is air dried after removal from the impregnation tank. A preferred treatment consists of air drying followed by baking in an oven at temperatures between 350° and 750° F. Such treatment results in formation of a dry, tough film. Treatment at about 750° F improves the film by a "sintering" effect.

Additional thicknesses of the fluorinated hydrocarbon surface above about 0.0002 or 0.0003 inch may be built up by spraying the fluorinated hydrocarbon polymer in a suitable vehicle onto the air dried coating prepared in the aqueous impregnation tank. The vehicle may be a fluid organic material in which the resin is dispersed and/or dissolved. The vehicle is preferably volatile. Aqueous dispersions are preferred. The particles utilized may be of the same order of subdivision utilized in the impregnation tank or they may be larger particles. The spraying operation may build up surface thicknesses of several mils. After the build up of the surface by spraying to the desired thickness, the article is preferably dried and heated in an oven

70

75

80

85

90

95

100

105

110

115

120

125

130

at between 350° F and 750° F as aforesaid.

The invention is illustrated in the following Example:—

5 An aluminum plate (Aluminum Company of America, 6061TG grade), 12"×12"×1/8" thick, having a stop-off coating on one surface, was cleaned by immersion in a mold caustic soda solution at 150° F for between 1½ and 1 minute. It was then rinsed and immersed in an aqueous nitric acid-chromic acid solution at room temperature for about 1 to 1 minute to remove the surface smut. The article was then rinsed. An oxide layer was applied or formed by making the article anodic in a tank containing 18 oz. per gallon sulfuric acid, 3.5 oz. per gallon of oxalic acid and a small amount of sugar. The bath was maintained at 30° F. The solution was agitated by passage of 1 cubic foot per minute of air per gallon of solution in the tank. The initial voltage was 18 volts, and the initial amperage was 28 amps. (equivalent to about 25 amps. per sq. foot). The current density was maintained at about this level throughout the oxidizing treatment by raising the applied voltage in about 1 to 2 volt steps every 2 minutes. After an applied voltage of 24 volts was reached, the voltage remained in the range 24—90 volts. The oxidizing process was terminated after 45 minutes. An oxide layer about 0.001 inch thick had been formed.

The article was then rinsed with air agitated cold water for 15 minutes and dipped into an impregnation tank containing one pound of polytetrafluoroethylene per 24 pounds of water. The polymer was dispersed in particles of about 0.2 microns. The impregnation tank was at a temperature of 160° F. At the end of 30 minutes, the article was withdrawn from the impregnation tank, air dried and then placed in an oven and baked at 400° F for 15 minutes. The resultant article had a polytetrafluoroethylene surface about 0.0003 inch thick. The surface was sound, slippery, and had superior properties.

The present invention may be applied to a specific article of use such as a frying pan generally identified by the numeral 10 in FIG. 1 of the accompanying drawings which are given by way of example only. FIG. 1 is a perspective view of the frying pan 10 with portions of the cooking surface thereof illustrating stages of treatment of the base metal of such frying pan. FIG. 2 is a cross-section of FIG. 1 as taken along lines 2—2 to enable a clearer illustration of the cross-sectional appearance of the article 10 to which the invention has been applied.

Referring now to the drawing, the frying pan 10 there shown is of conventional construction. It has a body 11 that is turned upward about its periphery to form a retaining rim 12. A handle 14 is connected to the rim 12 in the usual manner so that the

frying pan 10 may be easily manipulated. To enable an understanding of the invention, the cooking surface of the frying pan 10 has been divided into three sections 16, 18 and 20. FIG. 2 is a cross-section partially showing the details of the three treated surfaces 16, 18 and 20.

The surface 20 illustrates the base metal 11 of the frying pan 10 in its untreated condition. The surface 18 illustrates an intermediate stage of treatment of the base metal 11 whereby the intermediate layer 18 is formed as an absorptive, irregularly shaped, coarsely crystalline, porous oxide growth of the base metal. The portion 16 of the frying pan 10 shows the final treatment by a fluorinated resin in accordance with the invention.

The frying pan 10 was prepared by taking a conventional aluminum frying pan having the structural details above described. The undersurface 22 of the frying pan was protected with a stop-off composition so as to prevent its treatment in accordance with the invention. The interior portions 16 and 18 of the pan were treated in accordance with the steps of the invention. The portion 20 also had a stop-off composition applied to it to prevent its treatment. The portions 16 and 18 were treated by cleaning and forming the intermediate oxide layer thereon in accordance with the process of the previously described example relating to the treatment of aluminum. This resulted in the production of a coarsely crystalline aluminum oxide layer or surface 18 in which the crystals are identified by the numeral 24. This layer of surface was about 0.001" thick. When treated according to the invention, the pores formed between the crystals 24 appear to have absorptive properties that tend to rapidly soak up, like a sponge, liquids with which the same may come into contact. Thus, the portion 18 of the frying pan 10 illustrates the appearance of the intermediate layer that has been grown directly from the base metal, formed as an integral part thereof, and extends upward therefrom such that when any liquid material comes in contact with the same, the liquid is rapidly absorbed by the intermediate layer.

That portion of the pan 16 illustrated in the figures of the drawing was then treated by the resin impregnation steps of the foregoing example relating to the treatment of aluminum. As the resin 26 and the intermediate layer came into contact with each other, the resin was quickly absorbed in the pores formed between the crystals 24 of such layer. The result was the composite article shown at the portion 16 wherein the resinous material 26 is bonded directly to the surfaces of the irregularly shaped coarse crystals 24 of the layer 18, filling the interstices thereof and depositing an outer covering over both the

intermediate layer 18 and the base metal 11. In this way, the resinous material 26 became an integral bonded part of the intermediate layer 18 which itself was a direct growth and formation of the base metal and, therefore, inseparable from such base metal. In consequence, the resultant structure became a unitary or composite article from which neither the base metal 11, the intermediate layer 18 nor the resinous material 26 could be separated from each other. Scratch tests with sharp metal objects performed on the portion 16 of the frying pan 10 failed to lift, or tear away, or separate the resinous material 26 from either the intermediate applied layer 18 or the base metal 11.

The composite articles of the present invention have extremely adherent, tough and useful resin polymer surfaces. These articles show great resistance to corrosion. They have a very low coefficient of surface friction resulting in a high degree of lubricity. The aluminum composite articles contain the unusual combination of a highly corrosion resistant, slippery and abrasion resistant organic plastic surface, coupled with good surface hardness. It has unusually high heat transfer characteristics. It has excellent electrical resistance and resistance to radiation-caused degradation. Because of the process utilized in the preparation of these composite metal articles, it is possible to manufacture them with excellent surface finishes to close tolerances.

35 WHAT WE CLAIM IS:—

1. A process for producing a composite coated aluminum article having an aluminum base, an intermediate layer of aluminum oxide and an outer layer of a fluorinated hydrocarbon polymer, the process comprising:—

- (i) cleaning the surface of an aluminum substrate,
- (ii) anodically oxidising the cleaned substrate in an aqueous electrolyte containing from 15 to 18 ounces per gallon of sulphuric acid at a temperature from 25° to 40° F., at least one cubic foot of air per gallon of electrolyte per minute being passed through the electrolyte, the impressed voltage between the cathode and the aluminum anode being from 24 to 90 volts and the anode current density from 25 to 60 amps/sq. ft. the oxidation being continued until the oxide layer is at least 0.0005 inch thick.

(iii) immersing the oxidised aluminum in an aqueous suspension of a fluorinated hydrocarbon polymer the particles of said polymer being up to 2 microns in diameter, the suspension being at a temperature of at least 140° F., until the polymer fills the interstices of the oxide layer and forms an outer coating at least 0.0001 inch thick.

2. A process according to claim 1 in which the aqueous anodising electrolyte contains a carboxylic acid dissolved therein in a concentration equal to approximately 20% in the concentration of the sulphuric acid.

3. A process according to claim 2 in which the carboxylic acid is oxalic acid.

4. A process according to any of claims 1 to 3 in which the temperature of the aqueous anodising electrolyte is from 30° to 35° F. and the anode current density is from 25 to 40 amps/sq. ft.

5. A process according to any of claims 1 to 4 in which the temperature of the fluorinated hydrocarbon polymer suspension is from 160° to 190° F.

6. A method according to any of claims 1 to 5 in which the article is baked at a temperature of from 350° to 750° F. after the impregnation with the fluorinated hydrocarbon polymer.

7. A method according to any of claims 1 to 6 in which the anodic oxidation of the aluminum is continued until the oxide layer is at least 0.001 inch thick.

8. A method according to any of claims 1 to 7 in which the fluorinated hydrocarbon polymer is polytetrafluoroethylene.

9. A method according to any of claims 1 to 7 in which the fluorinated hydrocarbon polymer is a tetrafluoroethylene/hexafluoropropylene copolymer.

10. A process for producing a composite coated aluminum article substantially as herein described with reference to the Example.

11. A composite coated aluminum article made by a process claimed in any of claims 1 to 10.

12. A composite coated aluminum article according to claim 11 which is in the form of a cooking utensil.

13. An article according to claim 11 substantially as herein described with reference to the Example.

A. A. THORNTON & CO.,
Chartered Patent Agents,
Northumberland House,

303/306, High Holborn, London, W.C.1.

1069168

COMPLETE SPECIFICATION

1 SHEET

*This drawing is a reproduction of
the Original on a reduced scale*

FIG. 1

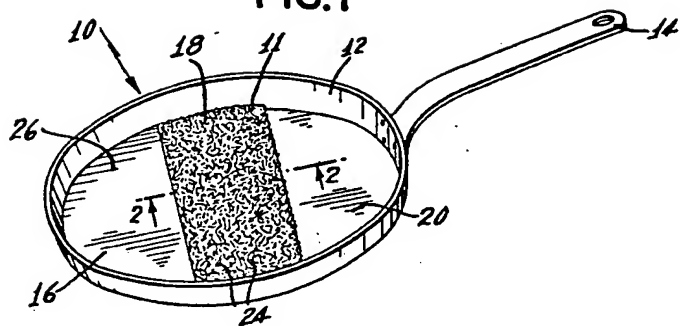
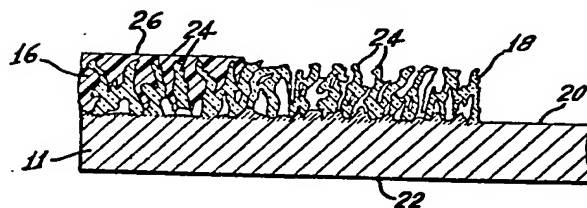


FIG. 2



THIS PAGE BLANK (USPTO)